Polymer 53 (2012) 5601–5618

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Feature article

Well-defined macromolecular architectures through consecutive condensation and reversible-deactivation radical polymerizations

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ARTICLE INFO

Article history:
Received 1 June 2012
Received in revised form
24 July 2012
Accepted 31 July 2012
Available online 14 August 2012

Keywords:
Condensation polymerization
Reversible-deactivation radical polymerization
Macromolecular engineering

ABSTRACT

This article highlights progress over the past decade in research on the preparation of controlled macromolecular architectures by means of sequential condensation and reversible-deactivation radical polymerizations. Such a dual approach for macromolecular engineering has become a subfield in itself over the years and is of great challenge for the development of advanced functional materials for targeted applications. Provided that conditions for adequate transformation chemistries and subsequent controlled polymerizations could be identified, physicochemical, mechanical, thermal and electrical properties of these complex macromolecules can be finely tuned by choosing and controlling the nature and length of the different polymer sequences together with molecular weight, composition and architecture of the copolymer.

1. Introduction

In the field of macromolecular engineering, most of the past research effort has been devoted to the production of block copolymers and more complex architectures from single or combined living/controlled polymerization methods [1,2]. Among the offered possibilities, reversible-deactivation radical polymerization (RDRP) [3], also known as controlled radical polymerization (CRP), could be originally combined with other types of controlled chain-growth processes, including living anionic [4–6] or cationic polymerizations [7] and ring-opening metathesis polymerization [8], thereby yielding well-defined polymer architectures with specific properties.

The access to well-defined copolymers comprising both polycondensate and polyvinyl segments (Fig. 1) is a technical challenge of another kind with numerous applicative stakes. Firstly, there is a recurring demand for engineering plastics with enhanced mechanical, thermal and surface properties. In particular, step-growth polymers like polyesters (PE), polycarbonates (PC), polyamides (PA), poly(ether ether ketone) (PEEK), poly(ether sulfone) (PES) and others possess better mechanical properties and thermal resistance than most of the addition polymers. In this field where polymers are often blended in order to adjust their end-use properties, novel block or graft copolymers with polycondensate segments may be needed as blend compatibilizers. Also, membrane technologies for fuel cell or filtration applications often use step-growth polymeric materials whose surface may benefit from specific hydrophilization or protein-repellent treatments. In order to address this issue, surface-initiated RDRP strategies have been proposed and will be described in a dedicated section. From the chemistry standpoint, the synthesis of complex polymer architectures like block and graft copolymers and polymer brushes from step-growth [9] and radical polymerization processes is rather difficult due to the very different nature of the respective polymerization mechanisms. Such combination requires the control of terminal, lateral or in-chain functionality of the polycondensate which can further activate a RDRP process.

The combination in one single macromolecule of rigid, sometimes poorly soluble and processable semi-conducting polymers synthesized by modern polycondensation routes and more flexible segments obtained by RDRP has been the subject of many recent studies. In this manner, various rod-coil copolymers [10] with excellent film-forming abilities and prone to microphase-separate have been obtained, together with tunable electronic, optoelectronic or fluorescent properties. In this approach, semi-conducting functional poly(*p*-phenylene vinylene) (PPV) [11] of controlled lengths, synthesized by Siegrist polycondensation [12] were considered. In the same way, tailor-made semi-conducting regioregular poly(3-hexylthiophenes) (rrP3HT) [13], polyfluorenes

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0032-3861
http://dx.doi.org/10.1016/j.polymer.2012.07.068

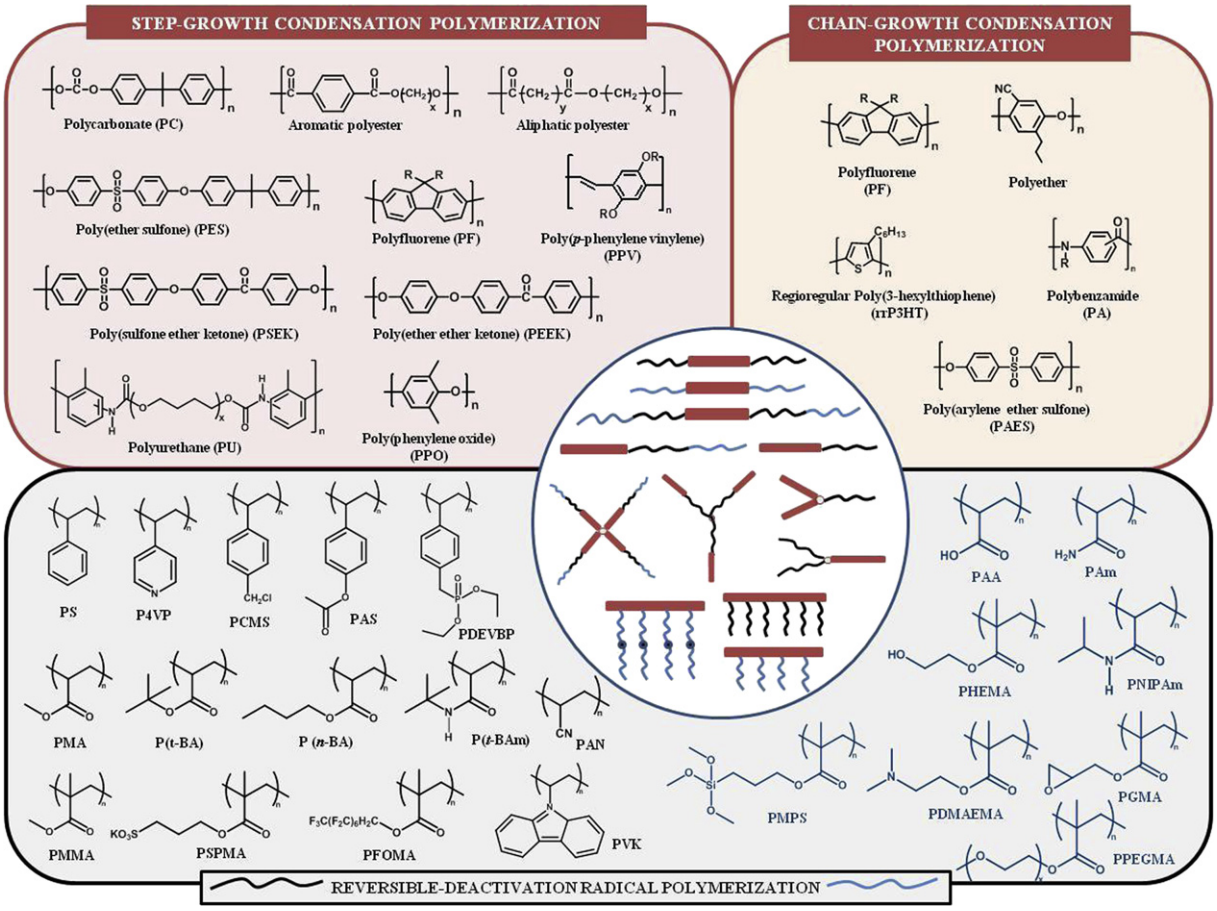


Fig. 1. General structures and macromolecular architectures obtained by the combination between condensation polymerization and RDRP.

(PF) [14] and poly(phenylene oxides) (PPO) [15] have rapidly emerged with the recent advent of chain-growth condensation polymerization [16]. Different strategies based on RDRP have been proposed to synthesize these rod-coil copolymers. Their synthesis and self-assembling properties in solution or in the bulk state will be illustrated.

In summary, a myriad of synthetic possibilities including either step- or chain-growth condensation and reversible-deactivation radical polymerizations were developed to obtain novel generations of well-defined copolymers. An exhaustive gallery of the different polymer building blocks and macromolecular architectures involved in this article is depicted in Fig. 1, and will be detailed in the following sections.

2. From step-growth condensation polymerization to RDRP

Throughout this article, *'traditional' step-growth condensation polymerization* (SGCP) is used to define the condensation reactions implying two difunctional monomers AA and BB. Other step-growth condensation mechanisms, such as Siegrist polycondensation, enzymatic self-condensation polymerization, transition metal coupling reactions, or depolymerization will be considered as '*non-traditional*' *SGCPs* [9].

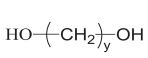
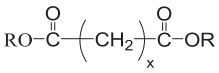
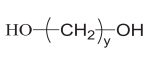
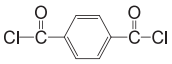
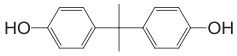
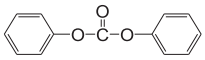
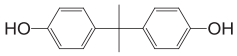
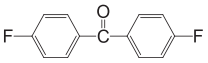
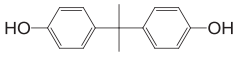
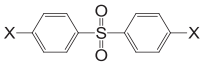
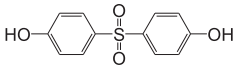
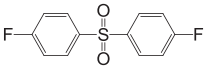
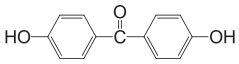
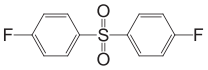
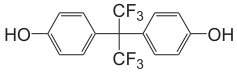
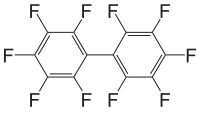
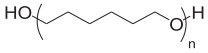
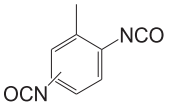
2.1. Preparation of ABA triblock copolymers with mid-block B derived from a traditional step-growth condensation polymerization

The monomer structures associated to the different traditional classes of SGCP involved in this section are reported in Table 1.

The crucial point for synthesizing well-defined triblock copolymers comprising a traditional step-growth condensation polymer as the mid-block is the controlled incorporation of RDRP functional groups at both chain ends of the polycondensate, which is essential for the success of the following RDRP step. Two different synthetic pathways presented in Scheme 1 proved their efficiency for preparing α,ω-telechelic macroinitiators. Method 1 represents the most often used approach through the chemical modification of end-groups. The polycondensate end-functionalities, mostly hydroxyl, were transformed into RDRP functional groups according to a one or two-step nucleophilic substitution mechanism. The second synthetic strategy (method 2 in Scheme 1) employs a functional chain stopper bearing both hydroxyl group and a functionality capable of activating RDRP such as a bromoisobutyryloxy [21] group for atom transfer radical polymerization [32] (ATRP) or a xanthate [19] for reversible addition fragmentation chain transfer polymerization [33,34]/macromolecular design by interchange of xanthates [35] (RAFT/MADIX) strategies. The chain stopper is directly incorporated in the step-growth polymerization process yielding the α,ω-telechelic macroinitiator in one single step [19,21].

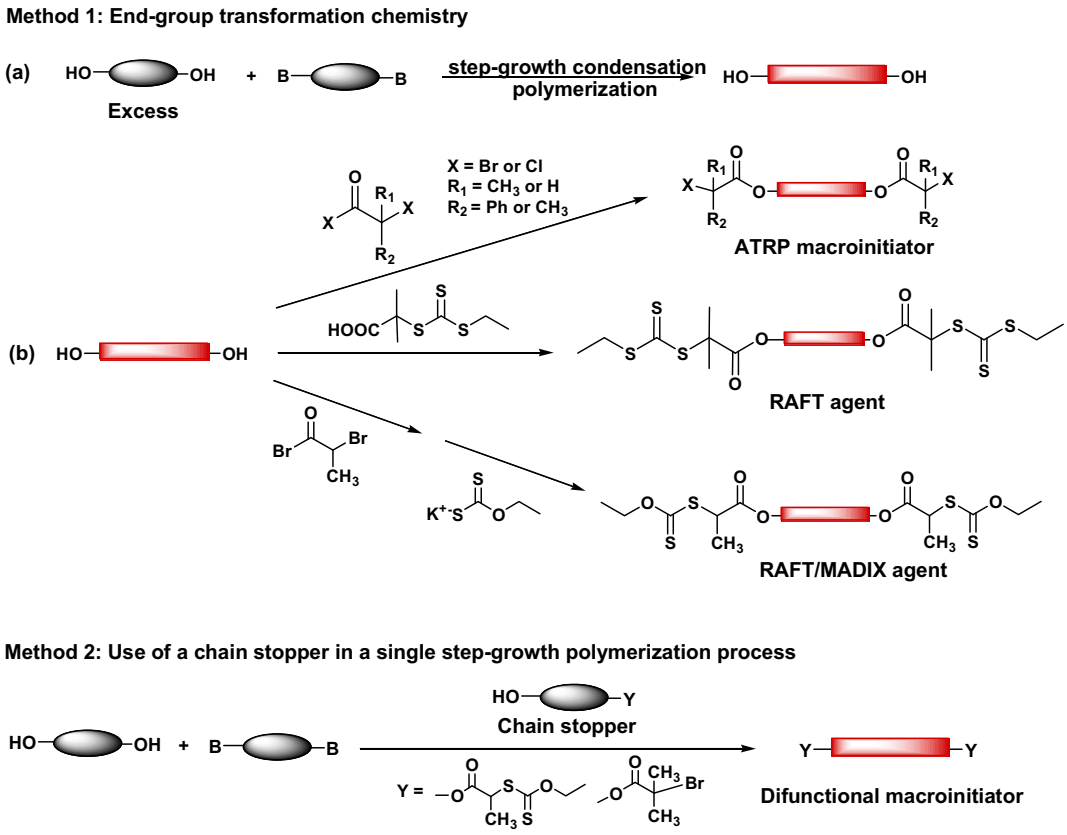
Surprisingly, in contrast to the numerous reports on ATRP approaches, RAFT polymerization from polycondensate precursors bearing thiocarbonylthio end-groups was never communicated before one recent contribution of our group. In this study we investigated both strategies for preparing a poly(butylene terephthalate) (PBT) macro-RAFT/MADIX agent [19]. The dixanthate-terminated PBT was successfully synthesized through both methods but it appeared to us that the use of a hydroxy-xanthate

Table 1
Chemical structure of difunctional monomers yielding α-ω-telechelic polymers by traditional step-growth condensation polymerization.

Entry	AA monomer HO—⬭—OH	BB monomer B—⬭—B	Step-growth condensation polymer	Reference
1			Aliphatic polyester R = H or CH_3	[17,18]
2			Aromatic polyester	[19]
3			Polycarbonate	[20,21]
4			Poly(ether ether ketone)	[22]
5			Poly(ether sulfone) X = F or Cl	[17,23–25]
6			Poly(ether sulfone)	[26]
7			Poly(sulfone ether ketone)	[27]
8			Fluorinated poly(arylene ether) (PAE)	[28]
9			Polyurethane	[29–31]

chain stopper was in that case the most suitable way. In contrast to the first method, the transformation chemistry of hydroxyl into xanthate groups was accomplished directly on the 1,4-butanediol monomer which was more environment-friendly in terms of reaction conditions. Indeed, the transformation reactions were operated at room temperature in tetrahydrofurane and acetone while the first method required the use of 1,1,2,2-tetrachloroethane at 65 °C due to the insolubility of PBT in conventional solvents at room temperature. More generally, the use of a chain stopper is an efficient way for combining two different types of polymerization without performing end-group transformation chemistry.

The controlled incorporation of RDRP functional end-groups at both chain ends of the polycondensate in method 1 is principally governed by step (a) in Scheme 1. In a traditional condensation polymerization, the nature of hydroxyl end-groups can be adjusted by introducing an appropriate excess of the diol monomer. Due to the difference in stoichiometry between AA and BB monomers, the targeted number-average molar mass M_n of the polycondensate block is limited according to the Carothers equation [36]. Difference between theoretical and experimental M_n values can also be imposed by the presence of transesterification or cyclization side reactions or by the high viscosity of the reaction mixture when step-growth polymerization is performed under melt-phase conditions [20]. Low M_n values (between 1000 and 8000 g mol^{-1}) were obtained for most classes of α,ω-telechelic step-growth condensation polymers reported in Table 1. The average number of hydroxyl end-groups can be determined by ^{1}H NMR spectroscopy provided that the corresponding signals can be distinguished from the rest of the spectrum [20]. Otherwise, Matrix-assisted laser desorption and ionization-time of flight (MALDI-TOF) mass spectrometry is a more sensitive method for revealing polymer end-groups [19]. The transformation of hydroxyl end-groups into ATRP functionalities was then readily accomplished mostly by a single nucleophilic substitution reaction. The reaction was performed in solution at room temperature for polycarbonate (PC) [20], poly(ether ether ketone) (PEEK) [22], poly(ether sulfone) (PES) [24] and poly(sulfone ether ketone) (PSEK) [27] segments with an appropriate excess of acyl halide derivative (approximately 3:1 relative to hydroxyl functionalities). ^{1}H NMR analyses confirmed the quantitative transformation of end-groups. Fourier transform infrared (FT-IR) spectroscopy can also be used for revealing as example the absorption peak at 1740 cm^{-1} attributed to the C=O



Scheme 1. Step-growth condensation polymerization strategies for the preparation of difunctional RDRP macroinitiators.

stretching vibration of the ester group and the extinction of the peak absorption of the phenolic end-groups at 3440 cm^{-1} [25]. Hydroxyl end-groups of the polycondensate were also converted into RAFT functionalities by esterification with a carboxy-functional trithiocarbonate-RAFT agent, namely S-ethyl-S′(α,α′-dimethyl-α″-acetic acid)trithiocarbonate [26]. More advantageously, two simple nucleophilic substitution reactions from commercially available reagents were necessary to convert the hydroxyl functionalities of PBT into *O*-ethyl xanthate (Scheme 1). The combination of NMR spectroscopy and MALDI-TOF spectrometry confirmed the quantitative yield of the two steps [19].

In method 2 depicted in Scheme 1, the nature of the polycondensate end-groups and the number-average degree of polymerization were governed by the stoichiometric ratio between the difunctional monomers and the chain stopper according to the Carothers equation [36]. Equality between the A and B functionalities concentrations was required to obtain a polycondensate with RDRP functional groups at both ends. The terminal incorporation of xanthate functionalities was ensured for different RAFT/MADIX-difunctional PBTs with molar masses values between 2000 and 6000 g mol^{-1} and low dispersities ($Đ$) [37] values ($1.27 < Đ < 1.64$) for a step-growth condensation process [19].

Examples of ABA triblock copolymers obtained from α,ω-telechelic polycondensate macroinitiators are reported in Table 2. Among all classes of conventional SGCPs, the employed RDRP technique for the incorporation of the radical segment such as polystyrene (PS) or polymethacrylates was mainly ATRP.

The efficiency of the ATRP macroinitiator in the controlled polymerization of the radical segment was largely illustrated. The controlled nature of ATRP of methyl methacrylate (MMA) and styrene (S) in diphenyl ether/*m*-xylene with a bifunctional chloro-telechelic polycarbonate macroinitiator was demonstrated by kinetic studies [20]. The nature of CuCl/ligand catalytic system and the temperature were optimized for each monomer. Triblock copolymers with high M_n values (until 100300 g mol^{-1} for PS-*b*-PC-*b*-PS by using tris(dimethylaminoethyl)amine (Me_6TREN) as ligand) and relatively low dispersities ($1.28 < Đ < 1.61$) were obtained. In addition, the quantitative consumption of the

Table 2
ABA triblock copolymers comprising a traditional step-growth condensation polymer as mid-block B and hydrophobic (entries 1–10, 14–15 and 17–18) or hydrophilic (entries 11–13 and 16) outer blocks A produced by RDRP.

Entry	Step-growth condensation mid-block B	Macroinitiator preparation method	RDRP technique	Outer block A	Reference
1	Aliphatic Polyester	Method 1	ATRP	PS	[17]
2	PBT	Methods 1 and 2	RAFT/ MADIX	P(*n*-BA)	[19]
3				P(*t*-BA)	[19]
4				P(*t*-BAm)	[19]
5	PC	Method 1	ATRP	PMMA	[20]
6				PS	[20]
7		Method 2	ATRP	PS	[21]
8	PEEK	Method 1	ATRP	PDEVBP	[22]
9	PES	Method 1	ATRP	P(*n*-BA)	[17,23,24]
10				PS	[17,23]
11				PPEGMA	[25]
12				PMAIpG	[25]
13		Method 1	RAFT	PPEGMA	[26]
14	PSEK	Method 1	ATRP	PS-*co*-PAN	[27]
15	Fluorinated PAE	Method 1	ARGET-ATRP	PSSA-*co*-PAN	[28]
16	PU	Method 1	ATRP	PDMAEMA	[29]
17				PS	[29,31]
18				PMMA	[30]

macroinitiator was also confirmed by size exclusion chromatography [20]. Pentamethyl diethylenetriamine (PMDETA) and Me_6T-REN appeared to be the most suitable ligands for the controlled polymerization of S and MMA under mild conditions, respectively [20]. Besides, a difunctional poly(ether sulfone) ATRP macroinitiator was capable of controlling the chain length of the poly(*n*-butyl acrylate) (P(*n*-BA)) outer blocks from 10000 to 75000 g mol^{-1} in the presence of the CuBr/$CuBr_2$/PMDETA catalytic system [24]. The triblock structure comprising a stiff central block incompatible with the outer blocks was investigated by small-angle X-ray scattering and mechanical spectroscopy. It was shown that the P(*n*-BA) block length had an important effect on the segmental, middle and terminal relaxations and can modify the properties of the super-soft state observed [24]. ATRP was also successfully applied for the controlled incorporation of poly(diethyl *p*-vinylbenzyl phosphonate) (PDEVBP) outer blocks from a α,ω-telechelic PEEK ATRP macroinitiator. The M_n and dispersities values of the obtained triblock copolymer were strongly dependent on the type of the ligand used to form a catalytic complex with CuBr. The system CuBr/PMDETA gave the best control of the DEVBP polymerization. The deprotection of the ethylphosphonate groups of PDEVBP into phosphonic acids led to very interesting electrolyte properties in the field of proton exchange membrane fuel cells [22].

The first example of the preparation of well-defined triblock copolymers comprising central block obtained by SGCP and various hydrophobic outer blocks grown through RAFT/MADIX polymerization was recently reported by our group [19]. The feasibility of the approach was shown with the preparation of a dixanthate-terminated PBT capable of controlling RAFT/MADIX polymerization of acrylates and acrylamido monomers [19]. These results undoubtedly open many synthetic possibilities considering the very large choice of monomer combinations offered by the RAFT/MADIX process mediated by *O*-ethyl xanthates [35].

In contrast, a moderate control of the RAFT polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) from a trithiocarbonate-functionalized PES was obtained, leading to large molecular weight distribution and bimodal traces in the size exclusion chromatography (SEC) response of the triblocks. It may be due to possible transfer reactions to PEG side chains or to the insufficient difference in stoichiometry between AA and BB monomers used during the preparation of the dihydroxy-terminated PES [26]. In that case, the hydroxyl functionality of PES can decrease significantly and give rise to a non negligible proportion of unreactive end-groups for the RAFT step [26]. More generally, low targeted M_n value of the polycondensate block, i.e. large excess of the AA monomer is required to prepare well-defined triblock copolymers with mid-block derived from a traditional SGCP.

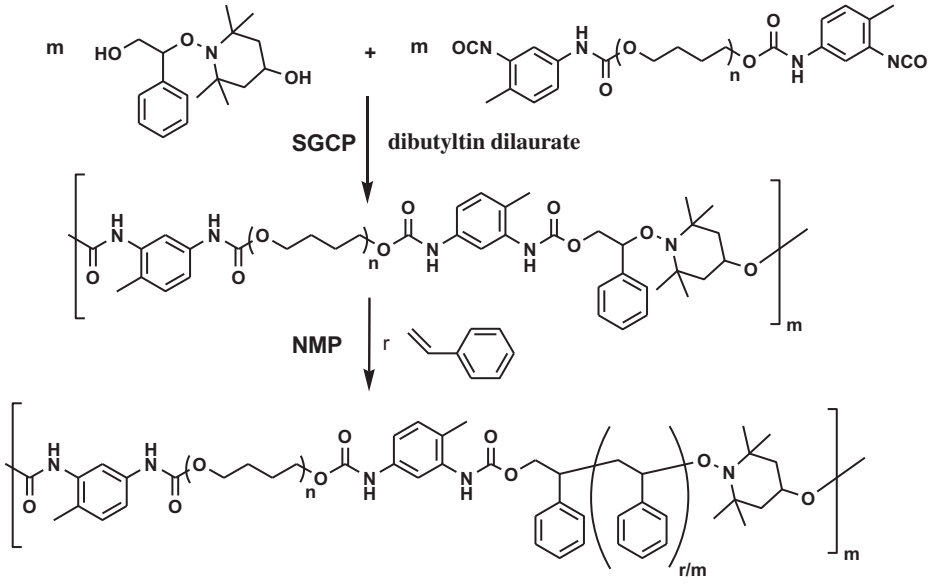
2.2. Preparation of multiblock copolymers comprising sequences resulting from a traditional step-growth condensation polymerization

An original approach, which is different from strategies presented in Scheme 1, was used to prepare multiblock copolymers comprising both polycondensates and controlled free-radical polymers. It consists in a SGCP between two difunctional monomers implying a monomer bearing the RDRP-active site as shown in Scheme 2. Alkoxyamine groups were incorporated in the polyurethane (PU) backbone by step-growth condensation reaction between tolylene-2,4-diisocyanate terminated poly(-tetramethylene oxide) (PTMO) and an alkoxyamine-based diol in the presence of dibutyltin dilaurate as catalyst [38]. The structure of the PU macroinitiator was confirmed by NMR and IR measurements. Well-defined polystyrene blocks were then incorporated by nitroxide mediated polymerization [39] (NMP) of S in a controlled manner in the PU segment leading to multiblock copolymers of PTMO and PS [38].

2.3. Preparation of block copolymers comprising a block derived from a non-traditional step-growth condensation polymerization

2.3.1. Polyesters

An alternative approach for controlling the terminal functionalities of polycondensates is to chemically degrade their main chain in a controlled fashion. For example, by adjusting the glycolysis conditions of poly(ethylene terephthalate) (PET), dihydroxy-terminated oligo(ethylene terephthalate glycol) (oligo(ETG)) (M_n = 700 g mol^{-1}) could be obtained [40,41]. The polymerization of S and a mixture of S/glycidyl methacrylate (90/10 and 80/20) was well-controlled by the derived dibromo-oligo(ETG) macroinitiator in anisole at 100 °C with the CuBr/(1,1,4,7,10,10)-



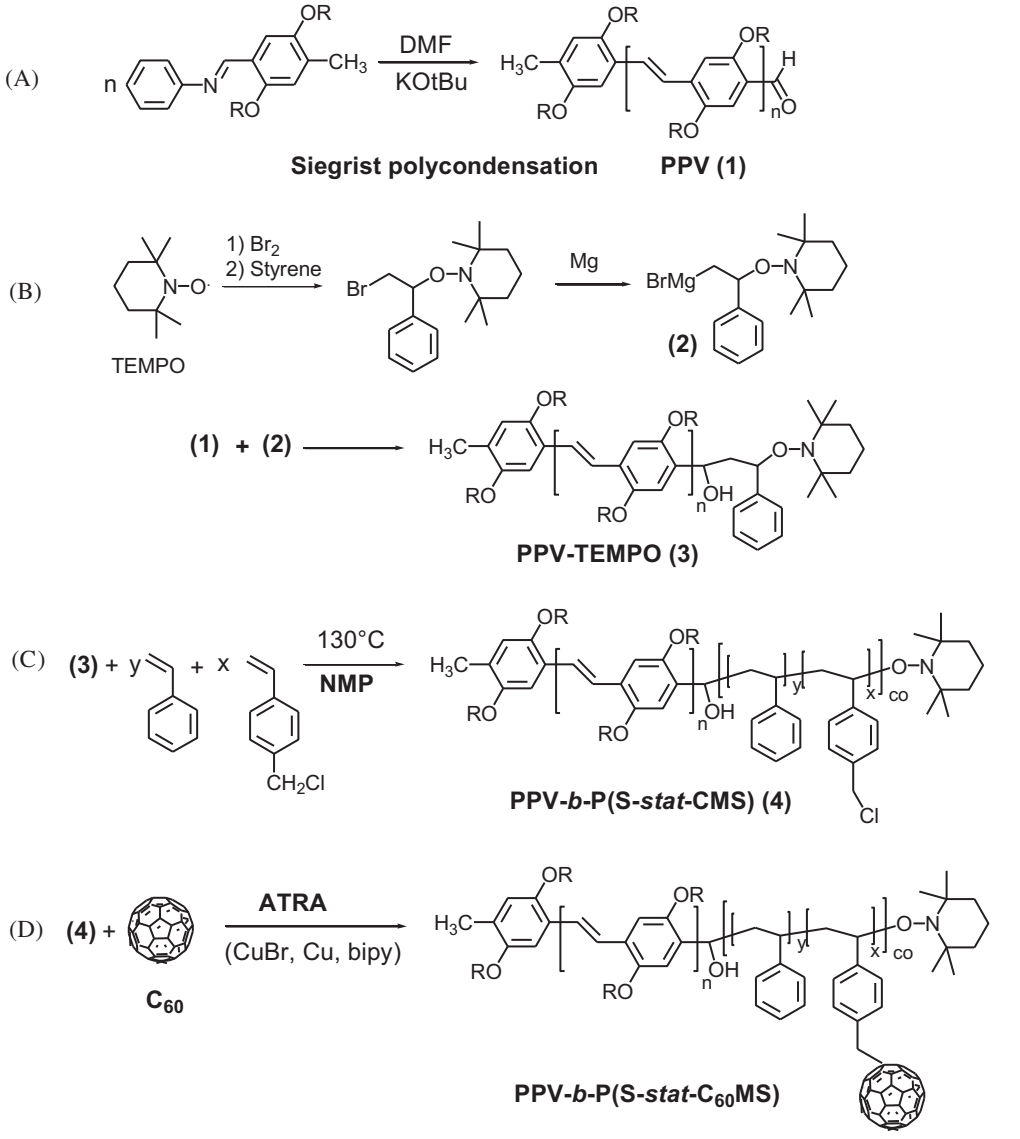
Scheme 2. Synthetic strategy for the preparation of multiblock copolymers made of PS and PU through consecutive SGCP and NMP of S [38].

hexamethyltriethylenetetramine (HMTETA) catalyst. Experimental M_n was close to the theoretical values and the dispersities decreased during the polymerization [40]. The enzymatic self-condensation polymerization of a hydroxy-acid monomer was used to prepare aliphatic polyesters bearing an hydroxyl functionality at one end and a carboxyl acid group at the other end. By combining this mechanism with a RDRP process, diblock copolymers comprising polyester could be obtained. Poly(10-hydroxydecanoic acid)-*b*-Polystyrene (P(HDA)-*b*-PS) was prepared by performing a self-condensation polymerization of HDA in presence of Novozyme-435 following by the chemical transformation of hydroxyl functionality into bromopropionate, with ATRP of S as the final step [42,43]. Beforehand, this approach requires the protection of the carboxylic end-group in order to avoid any detrimental interaction with the Cu(II) species.

2.3.2. Poly(paraphenylene vinylene)

Poly(paraphenylene vinylene) (PPV) and its derivatives are an important class of conjugated materials which exhibit excellent conducting and electroluminescent properties, thereby making them good candidates for light-emitting diodes or photovoltaic cells [11]. Such applications require dual electron-donating and -accepting ability. Hadziioannou et al. worked on the optimization of the photovoltaic efficiency of PPV by incorporating both donor and acceptor components such as C_{60} [44] in the polymer. They synthesized a series of rod-coil block copolymers using a combination between Siegrist polycondensation and NMP [45–51] or ATRP [52].

Monoaldehyde-functionalized poly(2,5-dioctyloxy-1,4-phenylene vinylene) (DOOPPV) selected as the rigid part in the copolymer was first prepared by Siegrist polycondensation [12,53]. The condensation of *para*-substituted methylbenzaldimines was realized under basic conditions (Scheme 3) leading to oligo-PPV with narrow dispersities. The aldehyde function was then transformed into the appropriate alkoxyamine functionality (e.g. TEMPO or TIPNO) suitable for controlling the polymerization of S [46] or *n*-BA [49] respectively. Experimental M_n values of DOOPPV, DOOPPV-*b*-PS and DOOPPV-*b*-P(*n*-BA) copolymers were determined by UV/vis absorption and NMR spectroscopies [46,49]. Kinetic studies confirmed the increase of experimental M_n values of the diblocks



Scheme 3. (A) Synthesis of PPV via Siegrist polycondensation. (B) Functionalization of PPV with TEMPO capping agent. (C) NMP of S and 4-CMS. (D) Acceptor-functionalization of the block copolymer. Adapted from the litterature [48].

during the NMP of both S and *n*-BA monomers. The incompatibility between the rod and coil blocks, which is necessary for their microphase separation, was then confirmed by transmission electron microscopy (TEM) [49]. The honeycomb structure of drop-casted solutions of the light-emitting DOOPPV-*b*-PS on glass slide after complete evaporation of the solvent was demonstrated by optical, fluorescence, atomic force (AFM) and scanning electron (SEM) microcopies [45,47] as shown in Fig. 2. These block copolymers spontaneously form micro-porous honeycomb structures with a regular geometry (Fig. 2A). The surface was then exposed to photo-oxidation (Fig. 2B) and aluminum vapor-deposition processes (Fig. 2C). Subsequently, a Scotch-tape was put on the aluminum-coated top layer (Fig. 2D) and removed (Fig. 2E). The unexposed polymer layer was then washed with chloroform revealing a hexagonally packed and very regular array of aluminum cups (Fig. 2G). These materials find their application in opto-electronics and photolithography.

Random copolymers with different ratios of S to 4-chloromethylstyrene (CMS) were also synthesized using the TEMPO-monofunctionalized DOOPPV as shown in Scheme 3. The incorporation of C_{60} was then achieved by employing atom-transfer radical addition (ATRA) of C_{60} to poly(4-CMS) [46]. The content of C_{60} grafted onto the flexible sequence of the block copolymer was governed by the feed ratio of CMS to S during the NMP process. Luminescence measurements confirmed the efficient electron transfer to C_{60} by the strong quenching of the luminescence from PPV block by C_{60} [46].

A similar approach was applied for preparing a series of novel fullerene-grafted donor-acceptor rod-coil diblock copolymers of PPV. The fullerene was grafted onto chloromethyl functionalities of the P(S-*stat*-CMS) [50] and P(*n*-BA-*stat*-CMS) [51] coil blocks through azidation which was monitored by IR and ^{1}H NMR spectroscopies.

2.3.3. Polyfluorene

Polyfluorene (PF) can be prepared by the condensation of bis-brominated monomers in the presence of the $Ni(COD)_2$ (COD = cyclooctadiene) catalyst through an intermolecular Yamamoto cross-coupling reaction. Hydroxyl-terminal groups of polyfluorene were incorporated by using an end-capper, such as 4-bromobenzyl alcohol (Scheme 4) [54–56]. This procedure corresponds to a step-growth mechanism where all end-groups of

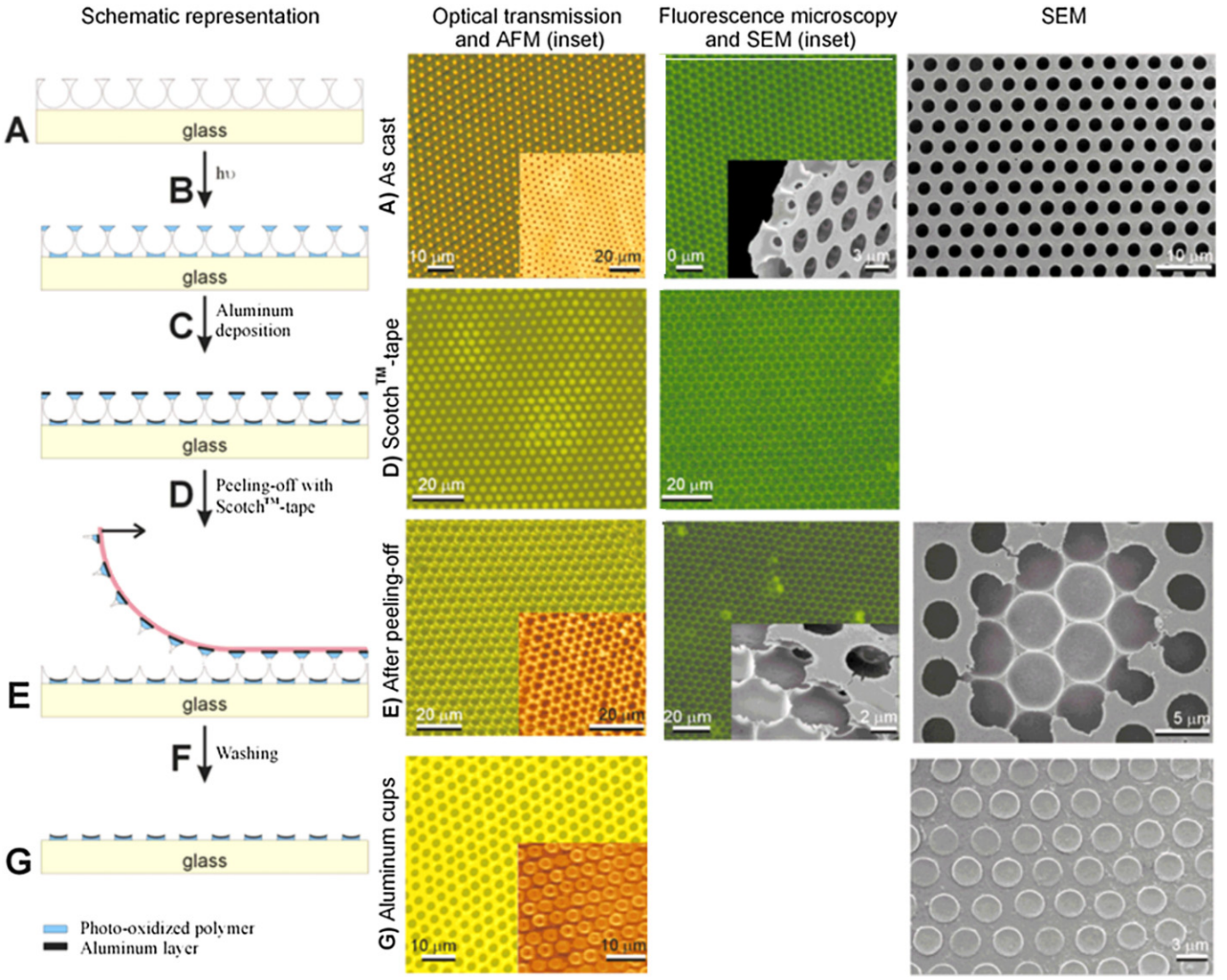
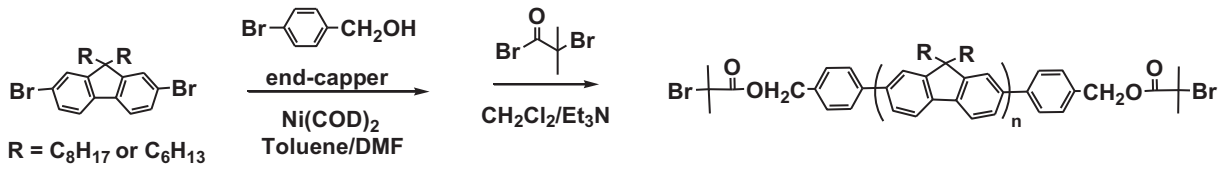


Fig. 2. Schematic representation, optical transmission microscopy, AFM, fluorescence microscopy and SEM images of DOOPPV-*b*-PS onto a glass slide (A) and after a specific chemical treatment (from B to G). Reproduced with permission from the literature [45].



Scheme 4. Synthetic approach to a polyfluorene-difunctional ATRP macroinitiator.

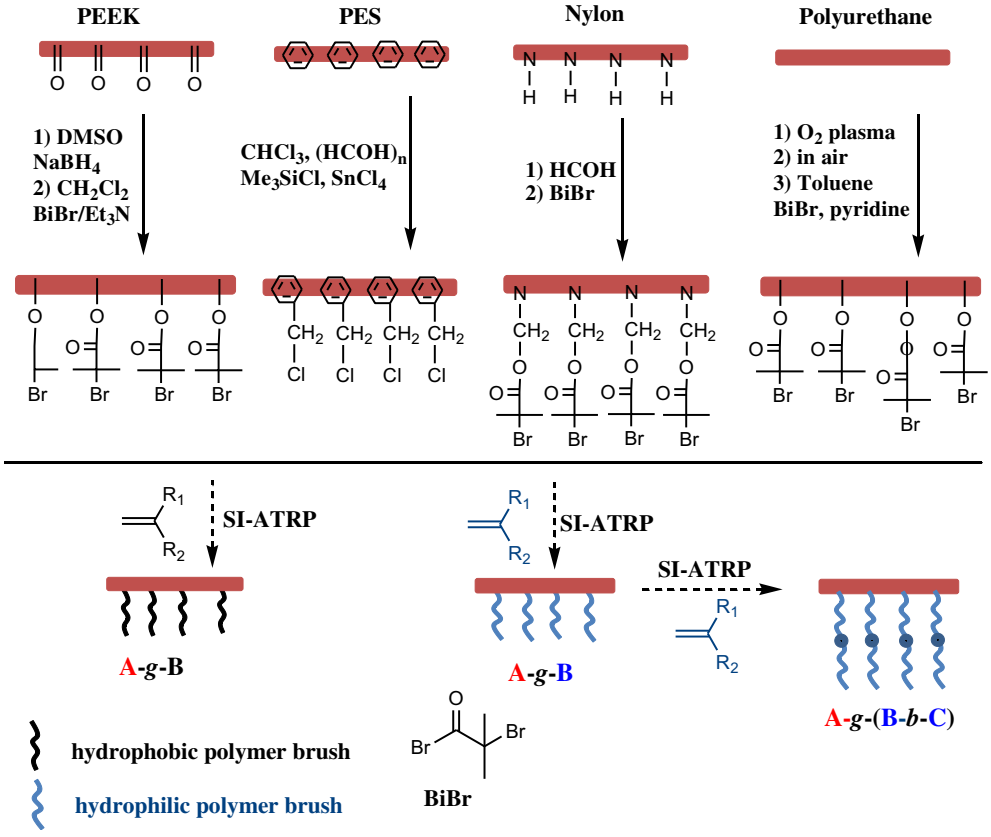
monomers and oligomers react together with the same probability, leading to a relative broad molecular weight distribution ($Đ = 1.6$) and limited M_n (around 4000 g mol^{-1}) [56]. The esterification of the dihydroxyl-terminated PF with 2-bromoisobutyryl bromide leads to the formation of dibromide-functionalized PF as shown in Scheme 4. The structure of the difunctional PFs was confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopies [56–59].

The controlled polymerization of several vinyl monomers was then conducted in the presence of the PF ATRP macroinitiator for preparing a series of well-defined coil-rod-coil triblock copolymers comprising PF as the rod segment and PDMAEMA (poly(2-dimethylamino)ethyl methacrylate) [56], PTHPMA (poly(2-tetrahydropyranyl methacrylate)) [57], PCzEMA (poly(2-(9-carbazoyl)ether methacrylate)) [58], PHEATMS (poly(2-triethylsiloxyethyl acrylate)) [59] or PNIPAm (poly(N-isopropylacrylamide)) [60] as coil segments. The efficiency of the PF macroinitiator in the ATRP process and the formation of well-defined triblock structures were confirmed by SEC, ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analyses. The linear first-order kinetic plots, linear dependence of M_n with monomer conversion during triblock copolymer synthesis and the low dispersity values obtained revealed the controlled nature of the polymerization [56,57]. Thermolysis following by hydrolysis of the PTHPMA segments and reaction of the PDMAEMA block with methyl iodide allowed the formation of amphiphilic triblock copolymers comprising a poly(methylacrylic acid) and a quaternized segment as coil blocks, respectively [56,57]. Aggregation of the PF segment occurred in aqueous solution as revealed by spectroscopic studies. The PHEATMS segment was also transformed into poly(cinnamoyloxyethyl acrylate) (PCEA) for photolithographic applications [59].

RAFT polymerization of NIPAm using a terfluorene-based dithioester was also used for the preparation of luminescent triblock copolymers comprising the water-soluble thermoresponsive PNIPAm as flexible outer blocks [61].

2.4. Preparation of polymer brushes from polycondensate surfaces

The grafting of polymer brushes from polycondensate surfaces is of great interest for tailoring the surface properties such as antifouling or stimuli-response properties. To this end, surface-initiated ATRP (SI-ATRP) [62] was used to prepare free-radical hydrophobic or hydrophilic polymer brushes from PEEK, PES, Nylon or PU surfaces. Prior to the SI-ATRP, ATRP initiation sites, such as chloromethyl or 2-bromoisobutyrate moieties, were introduced on the polycondensate backbone through different chemical reactions as shown in Scheme 5. Attachment of 2-



Scheme 5. Preparation of polymer brushes from polycondensate surfaces by SI-ATRP.

bromoisobutyrate initiating groups on PEEK-surface was performed by the sodium borohydride-assisted reduction of the PEEK keto to hydroxyl groups [63] followed by the esterification of the hydroxyl groups with 2-bromoisobutyryl bromide (BiBr) [64,65]. FT-IR [64,65] and X-ray photoelectron spectroscopy (XPS) [65] analyses confirmed the successful incorporation of the ATRP initiator. Chloromethylation was used to introduce $-CH_2Cl$ groups on the PES surface [66–70]. The reaction was mainly performed in chloroform by addition of paraformaldehyde, chlorotrimethylsilane and tin(IV) chloride and was controlled by FT-IR and ^1H NMR analyses [66,69]. The degree of substitution can be determined by comparison of the ^1H NMR signals of the two methylene protons of $-CH_2Cl$ related to the four aromatic protons next to the sulfonyl group [66]. Activation of amide surface groups with formaldehyde followed by the reaction between the resulting N-methylol polyamide and BiBr allowed the incorporation of ATRP initiators on the nylon membrane [71]. 2-bromoisobutyrate moieties were fixed to PU segments by oxygen plasma treatment of the surface followed by reaction with BiBr [72]. Another approach for anchoring reactive ATRP sites was recently proposed by Yameen et al. by deposing polyallylamine through pulse plasma polymerization on various types of polycondensate substrates (PEEK, PET and polyimide (PI)), which was then modified with BiBr to yield the ATRP surface initiators [73].

The polycondensate membrane was then prepared via a phase inversion process before processing the SI-ATRP. The chemical nature of the free-radical polymer brushes grafted via SI-ATRP from the different polycondensate surfaces is reported in Table 3. Most of them are hydrophilic to improve the hydrophilicity of the membranes. Poly(poly(ethylene glycol)monomethacrylate) (PPEGMA) was extensively studied due to its good antifouling effect. It was shown that the benzyl chloride groups of the PES afforded effective ATRP macroinitiators to grow well-defined polymer brushes [66]. XPS analyses were used to confirm the presence of grafted polymers [64,66,67,73]. Morphology changes of polycondensate surfaces were observed by AFM or SEM after the SI-ATRP step.

Hydrophilic brushes of poly(2-hydroxyethyl methacrylate) (PHEMA) and PPEGMA were grafted from 2-bromoisobutyrate moieties of nylon membranes in a controlled manner with observation of a linear increase in graft yields with polymerization time [71]. The dormant chain ends of the PHEMA and PPEGMA could be reactivated for SI-ATRP of both monomers PEGMA and HEMA respectively [71].

This kind of chemistry represents a stimulating field of investigation for the surface modification of membranes. In particular, improvement of hydrophilicity of PEEK, PES, PU or Nylon membranes can be realized through incorporation of PNIPAm, PPEGMA or PGMA brushes [64,66,67,71]. Water contact angle (CA) measurements were used to characterize the hydrophilicity of polycondensate surfaces as shown in Fig. 3C. Measurements of water CAs on the PEEK-*g*-PNIPAm surface revealed modification of water CAs from 42 to 87° by changing the temperature from 0 to 40 °C, i.e. above the lower critical solution temperature (LCST) of PNiPAm [64]. Due to the hydrophilic and thermosensitive nature of PNiPAm brushes grafted on PEEK surfaces, hydrophilicity of the polycondensate surface can be controlled by changing the temperature (Fig. 3C). Electrostatic interactions in the PEEK surface can also be tailored after grafting negatively charged polymer brushes such as poly(3-(methacryloxy)propane-1-sulfonate) (PMPS). The PEEK-*g*-PMPS surface interacted with the positively charged Rhodamine 6G dye. Change of coloration between initial PEEK segment/Rhodamine 6G and PEEK-*g*-PMPS/Rhodamine 6G was observed in aqueous solution (Fig. 3A) [64]. Surface antifouling properties of PPEGMA were demonstrated by comparing SEM images of pure PEEK (pristine PEEK) and PEEK-*g*-PPEGMA surfaces previously exposed to a culture of Escherichia coli bacteria. Presence of bacteria was observed on the PEEK surface whereas no bacteria were attached to the PEEK-*g*-PPEGMA surface (Fig. 3B) [64]. These results are of great promise for biomedical applications.

2.5. Preparation of graft copolymers by the combination of step-growth condensation and reversible-deactivation radical polymerizations

Graft copolymers comprising a polycondensate backbone and RDRP-derived side chains can be prepared through different strategies as shown in Scheme 6. One of them consists in the incorporation of lateral RDRP-functionalities in the polycondensate segment for subsequent RDRP grafting (*grafting from* methodology) [21,74–76]. To this end, chloromethylation or electrophilic Friedel–Crafts substitution reaction were used to introduce $-CH_2Cl$ active groups on the PES [74,75] and poly(ether sulfone ether ether ketone) (PESEEK) [76] segment respectively. Another possibility is to perform SGCP in the presence of a difunctional monomer bearing the lateral RDRP functionality [21] (Scheme 6) or another functionality which can be transformed into a RDRP functionality [77]. The degree of substitution can be controlled from peak integrations of ^1H NMR spectra and elemental analysis [21,74–76].

The functional polycondensates were then used as macroinitiators for the controlled polymerization of different radical monomers. The grafting density and backbone/side chain balance can be determined from the combination of different analyses and controlled by the reaction time of the ATRP of the selected monomer [74–76]. In particular the controlled character of NIPAm polymerization from chloromethylated PES backbone by using the CuCl/2,2′dipiridyl catalyst was demonstrated by a linear increase of the PNIPAm amount in PES-*g*-PNIPAm with the polymerization time [75]. Graft copolymerizations of MMA, methyl acrylate (MA) and *n*-BA catalyzed by $FeCl_2$/isophthalic acid were also successfully performed in DMF. M_n values increased with the monomer conversion and monomodal SEC traces of the different graft copolymers suggested the absence of side reactions in the ATRP process [74]. The copolymerization of sulfopropyl methacrylate (SPMA) was carried out from chloromethyl groups attached to

Table 3
Polymer brushes B and C grafted via SI-ATRP from the surface of polycondensate A.

Entry	Architecture	Polycondensate A	Block B and C	Reference
1	A-*g*-B (B hydrophobic)	PES	P4VP	[69]
2	A-*g*-B (B hydrophilic)	Nylon	PHEMA	[71]
3			PPEGMA	[71]
4		PEEK	PMPS	[64]
5			PNIPAm	[64]
6			PPEGMA	[64,65,73]
7		PES	PHEMA	[67]
8			PPEGMA	[66,67]
9			PGMA	[66]
10			PAm	[68]
11			PGAMA	[70]
12		PU	PPEGMA	[72]
13		PET	PPEGMA	[73]
14		PI	PPEGMA	[73]
15	A-*g*-(B-*b*-C) (B-*b*-C hydrophilic)	Nylon	PHEMA-*b* PPEGMA	[71]
16			PPEGMA-*b*-PHEMA	[71]
17		PES	PHEMA-*b* PPEGMA	[67]
18			PPEGMA-*b*-PHEMA	[67]

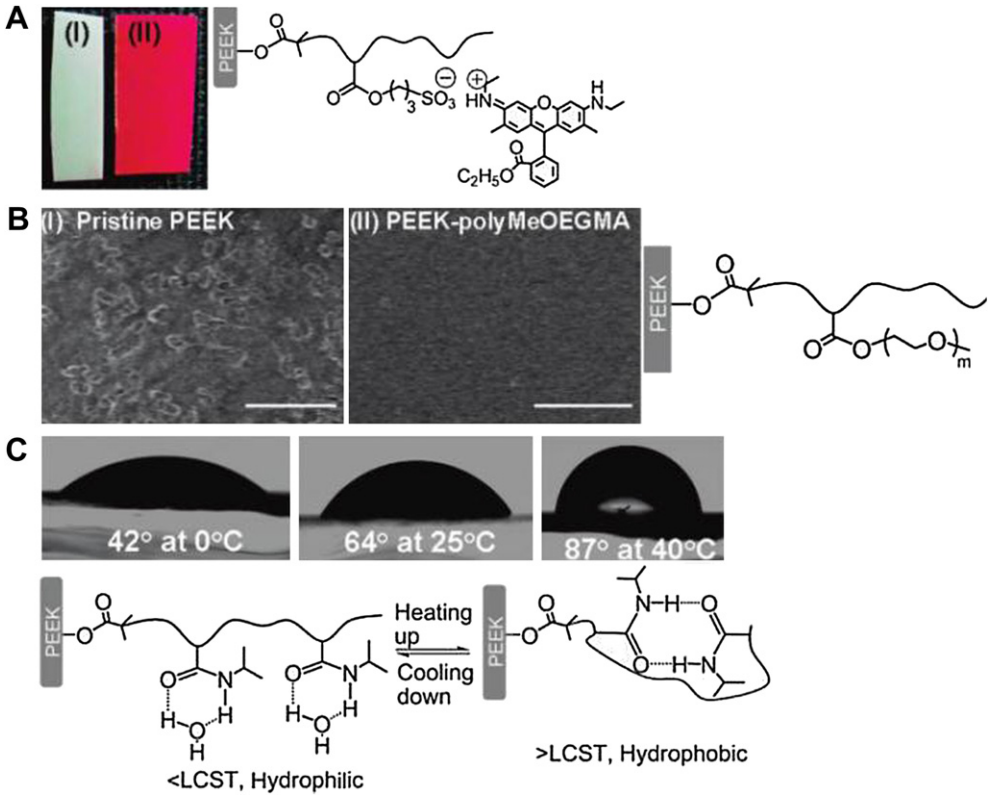
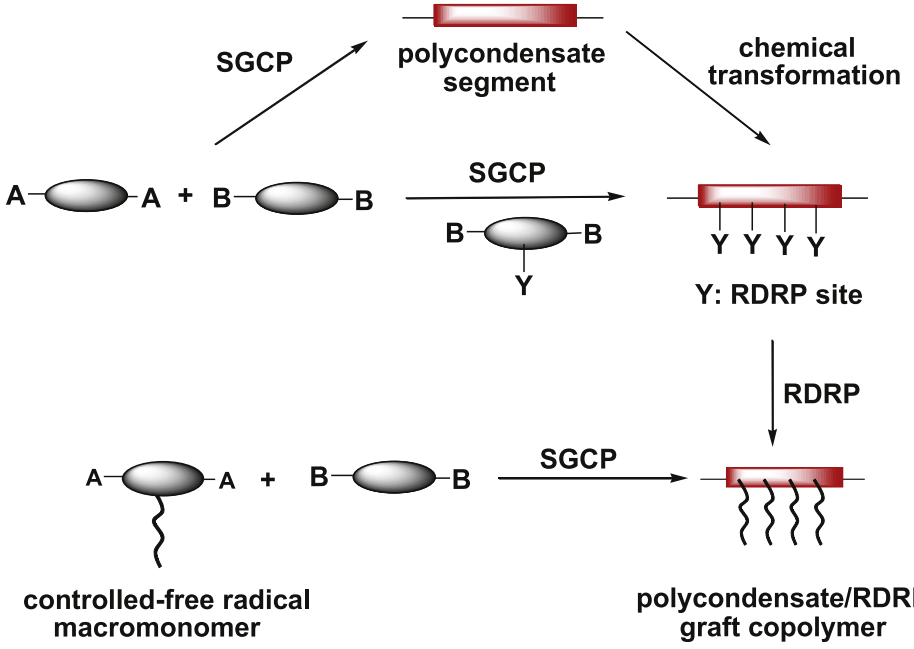


Fig. 3. Changes of PEEK surface properties by grafting polymer brushes via SI-ATRP. (A) Electrostatic interaction of pristine PEEK (I) and PEEK-*b*-PMPS (II) with Rhodamine 6G in aqueous solution. (B) SEM images of pristine PEEK and PEEK-*b*-PPEGMA surfaces previously exposed to an *E. coli* bacteria culture. Scale bars: 10 μm. (C) Water droplet profiles on the PEEK-*b*-PNIPAm surface at 0, 25 and 40 °C. Reproduced with permission from the literature [64].

PESEEK segment in DMSO with CuBr and HMTETA. The water uptake, proton conductivity and ion exchange capacity of the resulting PESEEK-*g*-PSPMA copolymers were modulated by the grafting polymerization time [76]. A PES macro-RAFT agent bearing trithiocarbonate-functionalities as lateral groups was used to control the polymerization of NIPAm and DMAEMA [77].

Cramail and co-workers proposed an original approach —whose general principle is presented in Scheme 6 for preparing PU-*g*-P(*n*-BA) copolymers. They synthesized a dihydroxy-P(*n*-BA) macromonomer via ATRP which was used as a reactive stabilizer in the SGCP between ethylene glycol and tolylene-2,4-diisocyanate in organic dispersed medium [78].



Scheme 6. Strategies for the preparation of graft copolymers comprising a polycondensate backbone and side chains derived from RDRP.

3. From chain-growth condensation polymerization to RDRP

The recent development of chain-growth condensation polymerization (CGCP) [16,79,80] has allowed the access to condensation polymers with well-controlled high molecular weights and narrow dispersities, in contrast to SGCP. This new concept consists in the enhancement of the reactivity of the polymer end-group compared with the one of the monomer AB so that the M_n values increased in proportion with the monomer conversion and that the functionalities should be controlled. Yokozawa and Yokoyoma have demonstrated that this living polycondensation process can be achieved by activation of the polymer end-group through resonance or inductive effects for *para*- or *meta*-substituted aromatic monomer respectively and by intramolecular catalyst transfers for Π-conjugated polymers [16,79,80].

The control of functionalities during the CGCP process combined with RDRP technologies enables the preparation of well-defined rod-coil block copolymers comprising condensation and vinyl polymers with various targeted architectures such as linear, graft and star-block copolymers. By choosing the appropriate chemical structure of the monomer and by controlling the rod-to-coil ratio, the mechanical, optical or electrical properties can be adjusted leading to various advanced functional materials. Besides, the self-assemblies of such rod-coil block copolymers constitute an emerging field in supramolecular chemistry since they provide novel nanostructures [10].

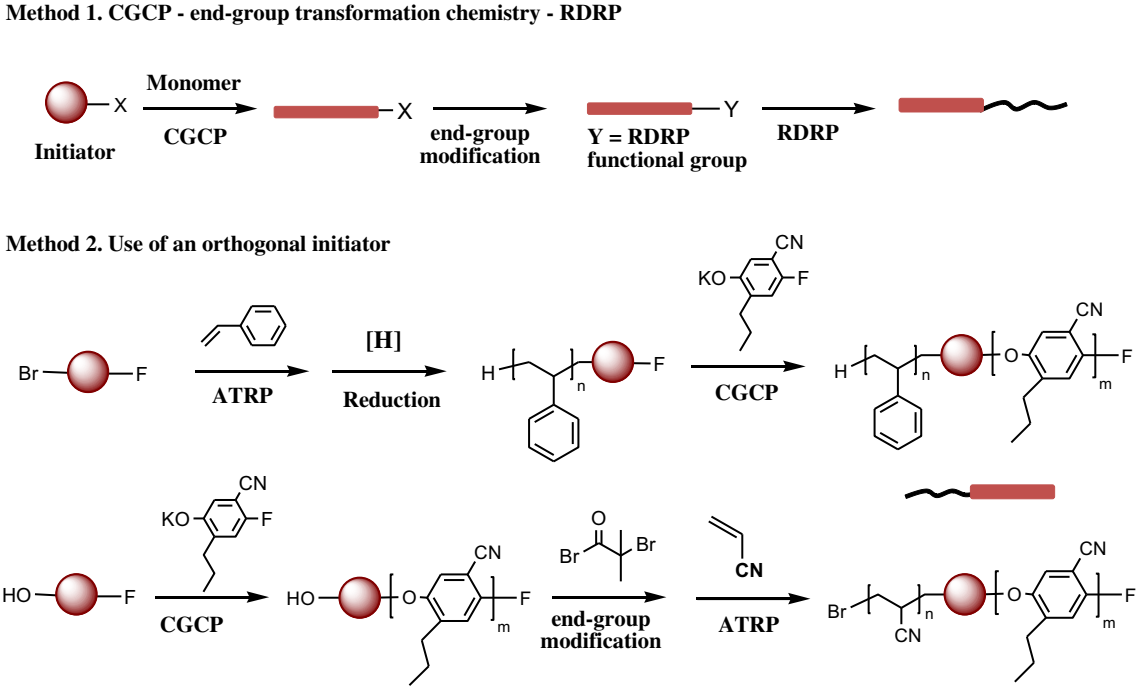
3.1. Synthesis of linear block copolymers

3.1.1. Para- and meta-substituted aromatic polymers as chain-growth condensation blocks

Due to their high selectivity, the *p*- and *m*-substituted aromatic monomers used in the CGCP preferentially react with the polymer end-groups compared to the other monomers, which confers a linear increase of the M_n values with monomer conversion and a living character to the CGCP.

Several approaches were used to prepare linear block copolymers comprising an aromatic block derived from CGCP like polyether or polybenzamide and polyvinyl blocks as presented in Scheme 7. A first approach is to perform the CGCP process followed by an appropriate end-group transformation chemistry to obtain the aromatic condensation polymer bearing the RDRP functionality. This strategy requires several steps between the two polymerization processes due to numerous chemical transformations. A more convenient strategy is the use of an orthogonal initiator bearing the functionalities for each kind of polymerization. A judicious choice of the chemical structure of the orthogonal initiator is required to avoid side reactions during the CGCP process such as transetherifications [81].

3.1.1.1. Polybenzamide. Yokozawa and co-workers have developed the synthesis of well-defined poly(N-octyl-*para*-benzamide) [82] and poly(N-octyl-*meta*-benzamide) [83] by CGCP with very low dispersities. They proved the controlled nature of the polymerization with a linear increase of the M_n values with the monomer conversion and the chain end control [82,83]. The combination of these CGCP mechanisms with RAFT [84,85], ATRP [86], or atom transfer radical coupling (ATRC) [87] of S has allowed the access to rod-coil block copolymers comprising the polybenzamide as the rod segment and the PS as the coil segment. The ATRP approach was investigated through the use of an end-capper bearing the ATRP functionality in the CGCP process [86]. Unfortunately, the reaction between the aminyl anion of the monomer generated during the CGCP process and the halogen atom of the initiator was observed and led to undesirable side reactions. In order to solve this problem, a different initiator bearing the protecting *tert*-butyldimethylsilyl (TBS) group was used in the CGCP of a series of N-octyl *m*- and *p*-benzoate monomer leading to the successful formation of TBS-functionalized polybenzamide. Deprotection of the TBS group followed by a reaction with BiBr led to the polybenzamide ATRP macroinitiator [86]. A dithiobenzoate chain transfer agent comprising a polybenzamide segment as the radical leaving group



Scheme 7. Synthetic methods used for the preparation of diblock copolymers by the combination of CGCP and RDRP.

R was prepared by performing firstly the CGCP of ethyl 3-(octylamino) benzoate monomer followed by a three- step modification procedure comprising deprotection, bromination and substitution reactions [84,85]. The obtained polybenzamide macro-RAFT agent proved his efficiency in the RAFT polymerization of S leading to diblock copolymers with controlled M_n and low dispersities ($Đ < 1.30$) [84,85].

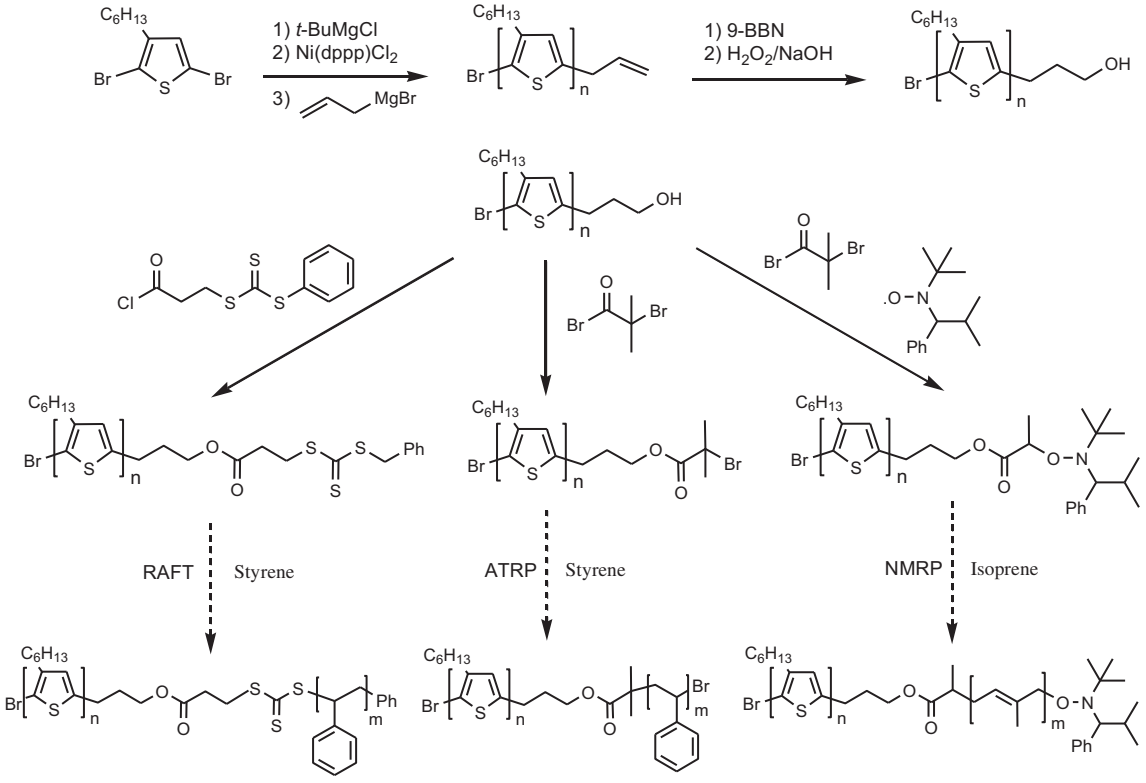
3.1.1.2. Polyether. The first method in Scheme 7 was employed for the synthesis of block copolymers containing trifluoromethylated poly(phenylene oxide) [88]. CGCP of the 4-fluoro-4-(trifluoromethyl) phenolate monomer in the presence of the appropriate initiator was firstly performed followed by the introduction of the ATRP moiety at chain ends and the controlled homopolymerization of S and MMA [88]. The preparation of well-defined diblock copolymers comprising PS as the radical segment and poly(1-cyano-4-propyl-2,5 phenylene oxide) as the polyether segment was successfully accomplished by using the orthogonal initiator approach [81]. The 4-(1-bromoethyl)-4′-fluorobenzophenone firstly initiated the ATRP of S in presence of CuCl/4,4′-dinonyl-2,2′-bipyridyl (bpy 9) catalytic system, leading to the formation of the PS block. The reduction of the C–Br bond was then performed before carrying out the CGCP of the potassium 5-cyano-4-fluoro-2-propylphenolate monomer (M) [81]. This approach was not suitable for the synthesis of poly(acrylonitrile)-*b*-polyether copolymer due to the decomposition of the PAN backbone at the CGCP temperature ($T = 120$ °C) [89]. In order to circumvent this limitation, the order of polymerization was reversed, i.e. CGCP of monomer M was followed by the ATRP of AN [89]. The hydroxy group of the orthogonal initiator remained stable during the CGCP process and could be converted later into an ATRP initiator group after reaction with BiBr (Scheme 7) [89].

3.1.2. Π-conjugated polymers as chain-growth condensation blocks

3.1.2.1. Polythiophene. Due to their excellent electrical conductivities, light-emitting abilities and high-field effect mobilities, regioregular poly(3-hexylthiophenes) (rrP3HT) have received much attention in recent years for the conception of solar cells, light-emitting diodes or field effect transistors [13]. However, this polymer has poor mechanical and processing properties in comparison to flexible polymers. These properties can be tuned by the incorporation of appropriate polymer blocks into the polythiophene chain through RDRP techniques such as ATRP, NMP and RAFT. Optical and electrical properties of block copolymers comprising rrP3HT can also be adjusted by changing the ratio between the conducting and non-conducting segments.

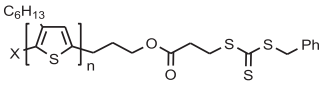
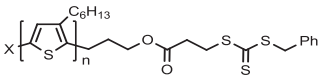
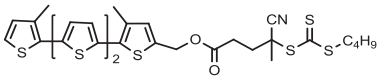
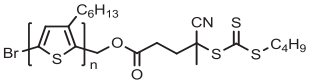
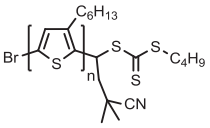
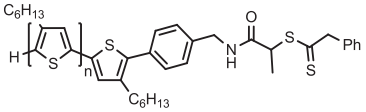
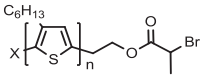
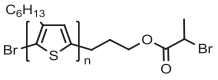
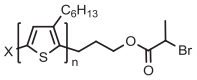
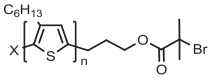
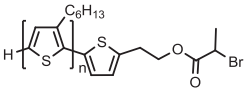
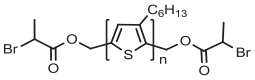
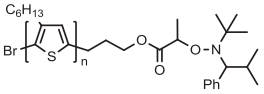
The synthesis of rrP3HTs was developed by McCullough and coworkers through the Grignard Methatesis (GRIM) method [90–92]. McCullough's [93,94] and Yokozawa's groups [79,95] demonstrated that catalyst transfer condensation polymerization followed a CGCP mechanism with living characteristics. They proved that the M_n can be predicted by the molar ratio of monomer to the Ni(dppp)Cl_2 nickel initiator (dppp = 1,3-bis(diphenylphosphino)propane). The living character of GRIM polymerizations allows the synthesis of various end-functionalized rrP3HT through the *in situ* addition of allyl magnesium bromide to the nickel-terminated rrP3HT [96,97] as shown in Scheme 8. The allyl end-group can be converted into hydroxypropyl by hydroboration/oxidation which can be readily transformed into RDRP-functionalities (Scheme 8), leading to different possibilities for the preparation of block copolymers comprising rrP3HT segments. A detailed review dealing with the synthesis of such block copolymers was published during the preparation of our article [98].

The polythiophene macro-RAFT, -NMP and -ATRP agents used for the incorporation of the radical block are presented in Table 4.



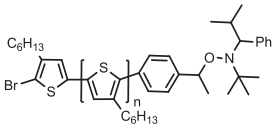
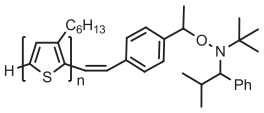
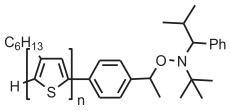
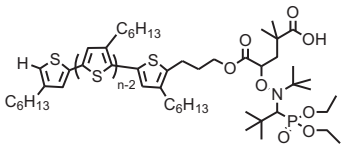
Scheme 8. Preparation of regioregular poly(3-hexylthiophene) RDRP macroinitiators.

Table 4
Polythiophene macro-RAFT (entries 1–11), ATRP (entries 12–22) and NMP (entries 23–26) agents used for the preparation of rrP3HT-polyvinyl block copolymers.

Entry	Macro-RDRP agent (X = Br or H)	Monomer	Reference
1		S (X = Br)	[99]
2		S + acrylate (X = H)	[100]
3		NVK	[101]
4		4VP	[102]
5		S	[103]
6		AA	[103]
7		MA	[103]
8		MMA	[103]
9		S	[103]
10		S	[103]
11		Perylene diimide acrylate	[104]
12		MA (X = H or Br)	[105]
13		*t*-BuA (X = H or Br)	[105]
14		FOMA (X = Br)	[106]
15		*t*-BA	[107]
16		MA (X = H or Br)	[108]
17		S (X = Br)	[109]
18		MMA + HEMA (X = H)	[110]
19		MA	[111]
20		S	[111]
21		MA	[111]
22		S	[111]
23		I	[99]

(*continued on next page*)

Table 4 (*continued*)

Entry	Macro-RDRP agent (X = Br or H)	Monomer	Reference
24		*n*-BA + CMS	[112]
25		Perylene diimide acrylate	[113]
26		S	[114]
27		S 4VP MA MMA MA + 4VP I	[115]

Among the examples of RAFT copolymerization, 'Z'-connected rrP3HT block copolymers were prepared using trithiocarbonate-RAFT agents (entries 1–4) and 'R'-connected rrP3HT block copolymers were prepared using trithiocarbonate- (entries 5–10) or dithioester- (entry 11) RAFT agents. Bromoester terminated-rrP3HTs were employed as ATRP macroinitiators. rrP3HTs functionalized with a TIPNO alkoxyamine end-group were prepared and used in the NMP of S derivatives, acrylates and isoprene (entries 23–26).

The incorporation of coil blocks such as PS [99,109,111], polyisoprene [99], PMA [105,108,111], poly(*tert*-butyl acrylate) [105] or poly(fluorooctyl methacrylate) [106] from the polythiophene macro-RDRP agents resulted in the formation of block copolymers soluble in many organic solvents and having film-forming properties. The solid state morphology of thin films of these materials, prepared by drop-casting from organic solution followed by the evaporation of the solvent, was investigated by tapping mode atomic force microscopy (TMAFM) or by TEM. The analyses revealed the formation of a nanofibrillar morphology [99,106,108,109,111]. The conductivity of such diblock copolymers was adjusted by the molar ratio of the conducting P3HT block to the non-conducting block [99,105,109,111].

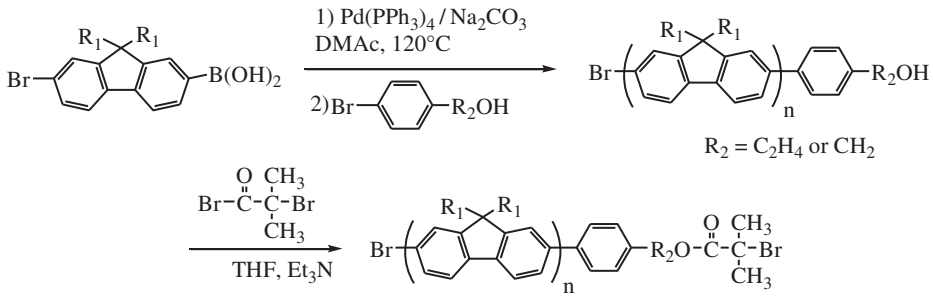
Donor-acceptor polythiophene block copolymers were obtained according different approaches. One of them is the linkage of a fullerene-group like C_{60} to chloromethylstyrene units [112] or a carboxylic acid-functionalized fullerene to HEMA units [110]. On the other hand, the direct RDRP of a monomer containing electron acceptor groups such as the perylene diimide acrylate [104,113] or N-vinylcarbazole (NVK) [101] may lead to interesting properties for solar cells and organic light-emitting diode applications, respectively.

The preparation of rrP3HT-based graft copolymers was recently successfully accomplished by Hadziioannou and co-workers [116]. ω–acrylate- and methacrylate-P3HT were first obtained from the ω-hydroxyl-terminated P3HT [105] by reaction with (meth)acryloyl chloride. The NMP of the P3HT macromonomers was then performed in the presence of *n*-butyl acrylate as comonomer and the Blocbuilder alkoxyamine. The preparation of graft copolymers of P3HT and P(*n*-BA) was shown by NMR and SEC analyses. Although 29% of the P3HT macromomer wasn't incorporated in the graft copolymer, this original approach promises very interesting results to obtain well-defined graft copolymers based on P3HT [116].

3.1.2.2. Polyfluorene. Monohydroxy-functional polyfluorenes can be prepared through the Suzuki-Miyaura coupling polymerization in the presence of tetrakis(triphenylphosphine)palladium(0) and an end-capper as shown in Scheme 9. Yokozawa et al. also confirmed the existence of a CGCP mechanism for the Suzuki-Miyaura cross coupling polymerization [16]. The esterification of the obtained polymer with the dibrominated compound (BiBr) afforded the final ATRP macroinitiator (Scheme 9).

PF-containing rod-coil block copolymers show a great interest due to their high thermal/chemical stability and excellent fluorescence quantum yields. Examples of rod-coil block copolymers derived from the polyfluorene ATRP macroinitiator are reported in Table 5.

Such block copolymers provide novel multifunctional sensory materials due to their very interesting self-assembling properties. Different nanostructures depending on the temperature, solvent composition or pH-solution [10,117,119,120] were obtained and characterized. Morphological transformation in solution was observed for the first time for a fluorene-based rod-coil block copolymers with amphiphilic PF-*b*-PAA (poly(acrylic acid)) [117]. The study was performed in a mixture of dichloromethane, a common solvent for both blocks, and methanol chosen as the selective solvent for PAA block. By changing the methanol content and PAA block length, different morphologies were observed by TEM, like lamellae, spheres, micelles, vesicles or cylinders due to



Scheme 9. Synthetic approach to a mono-functional polyfluorene ATRP macroinitiator.

the modification of the interfacial tension between the PF core and PAA corona [117]. Similar modifications of the polymer morphology through the coil selective solvent were observed with PF-*b*-PTMSPMA (poly(3-trimethoxysilyl)propyl methacrylate) [120] and PF-*b*-PDMAEMA [119]. The PDMAEMA block is both temperature- and pH-responsive. It was shown that the LCST of the PF-*b*-PDMAEMA decreased by increasing the pH-solution. The PDMAEMA chains in the corona were almost depronated and aggregated at higher pH.

As presented in Fig. 4, the photoluminescence intensity of 0.1 wt% PF_7-*b*-$PDMAEMA_{45}$ in water strongly varies with pH value and temperature, suggesting that these copolymers behave as on/off fluorescence indicators of temperature and pH.

3.2. Synthesis of non-linear block copolymers

Non-linear block copolymer such as miktoarm star and star-block copolymers exhibit interesting self-assembling properties, which can be different from the corresponding diblock copolymers depending on the chosen solvent.

The orthogonal initiator approach used for preparing linear diblock copolymers (Scheme 7) was investigated in the synthesis of miktoarm star copolymers (Scheme 10a). Depending on the structure of the trifunctional orthogonal initiator, different architectures were targeted. AB_2 and A_2B and $(AB)_3$ star copolymers of aromatic polyether (B) and PS (A) were successfully synthesized [125,126]. ATRP of S was firstly accomplished by initiation with brominated moieties and was followed by the CGCP of the potassium 5-cyano-4-fluoro-2-propylphenolate monomer on the fluorinated end of the preformed PS to obtain AB_2 and A_2B structures [125] (Scheme 10a). A tribromo-initiator was used to prepare $(AB)_3$ star-block copolymers (Scheme 10b) [126]. ATRP of S with CuBr/bpy9 was first performed, followed by the transformation of bromide functionalities into azido groups. At this stage, two synthetic strategies were evaluated. A click reaction was used in the presence of 4-[(3-butyn-1-yloxy)-methyl]-4′-fluorobenzophenone to prepare the macromonomer bearing a fluorinated end which was allowed to activate the CGCP process. However due to the partial efficiency of the initiation sites, this strategy generated a small amount of one- and/or two-arm star polymers. At the other end, the click chemistry performed between the azide-terminated PS and the alkyne-terminated aromatic polyether led to the corresponding 3-arm star diblock copolymers of polyether and PS without by-products as shown in Scheme 10b [126]. The self-assembling properties of this kind of star copolymers were compared to those of their linear counterparts. Whereas the polymer structure had no effect on the aggregates morphology in THF, the self-assembled structures were different in a mixture of THF and methanol. A_2B type miktoarm star copolymer afforded spherical aggregates similar to those obtained from THF solution. In contrast, the AB diblock and $(AB)_3$ star-block copolymers self-assembled to both give disordered aggregates and AB_2 type miktoarm star copolymer showed a fiber-like structure [125,126].

Amphiphilic star-shaped rod-coil diblock copolymers composed of PAES units in the core and poly(2-2(methoxyethoxy)ethyl methacrylate-*co*-oligo(ethylene glycol)methacrylate) (poly poly(-MeO_2MA-*co*-PPEGMA)) units in the shell were synthesized through a similar strategy in the presence of a 4-arm initiator (Scheme 10(c)). Their micellar properties in aqueous solution were evaluated. Fluorescence spectroscopy confirmed the unimolecular behavior in the encapsulation of Nile Red [127].

Table 5
AB and ABC di- and triblock copolymers comprising a PF rod block A and B and C coil blocks derived from ATRP.

Block A — R_1	Polymer B	Polymer C	Ref.
C_6H_{13}	PAA		[117]
	PNIPAm		[118]
	PDMAEMA		[119]
	PTMSPMA		[120]
C_6H_{13}	PPEGMA	POPS	[121]
C_8H_{17}	PMPSPMA		[122]
$C_3H_6NC_2H_9$	PNIPAm		[123]
	PMMA		[124]

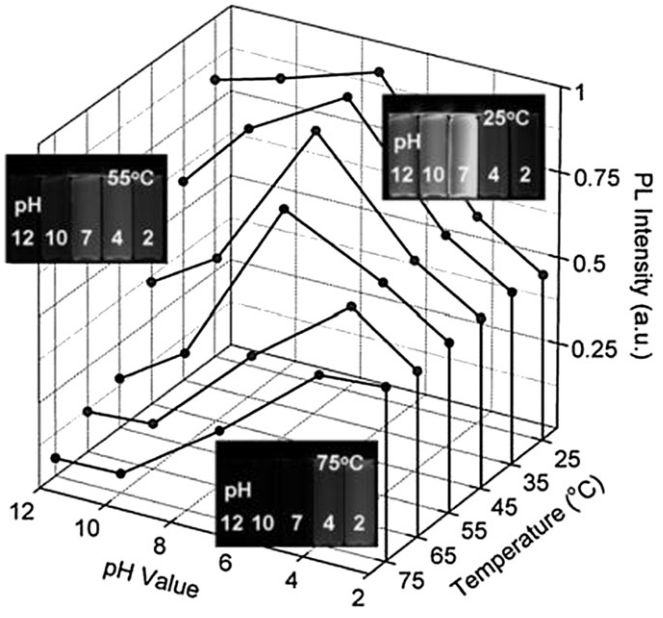
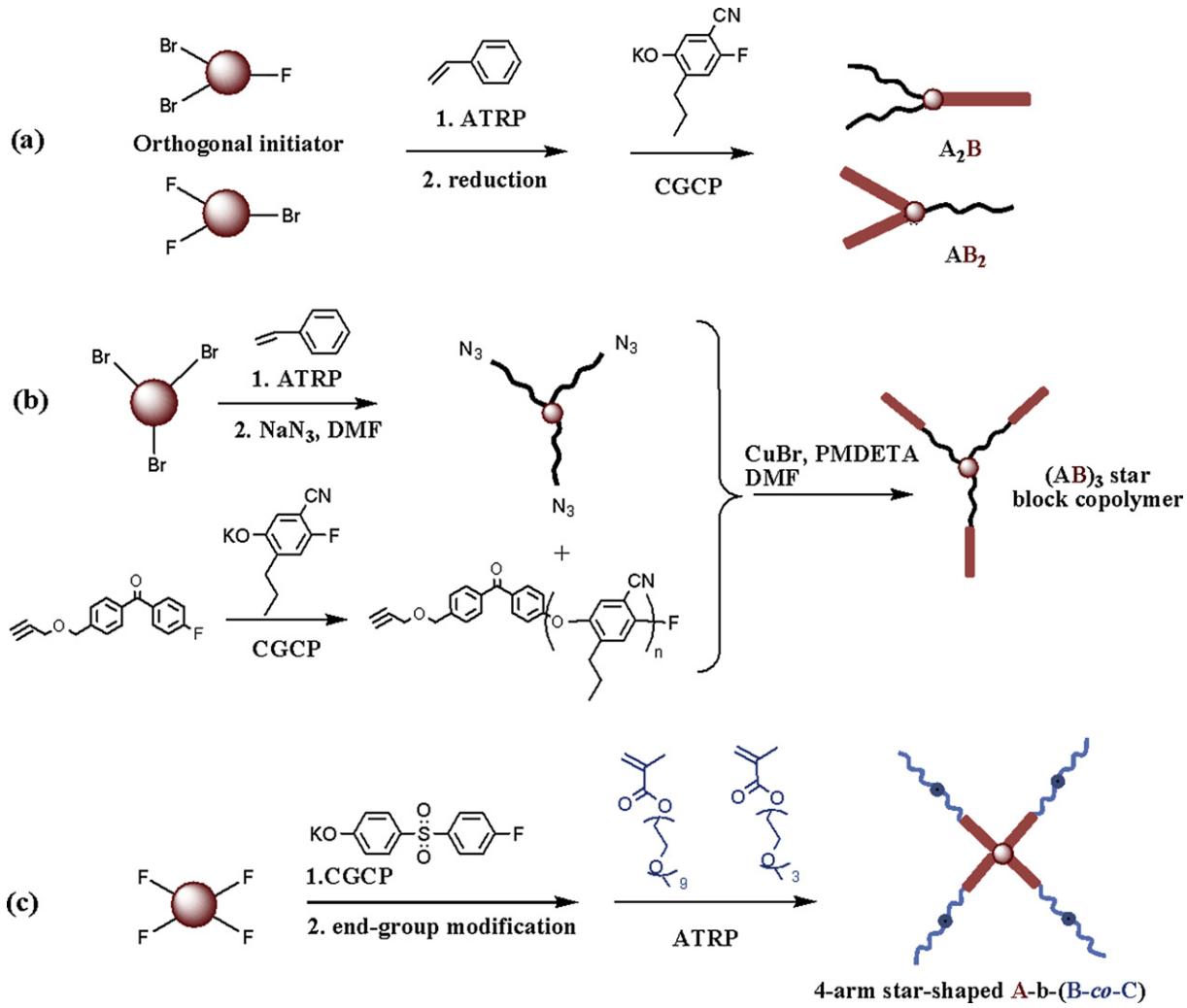


Fig. 4. Three-dimensional plot of the variation of photoluminescence intensity (PL intensity) with temperature and pH. Reproduced with permission from the literature [119].



Scheme 10. Strategies for the preparation of non-linear block copolymers. (a) Preparation of AB_2 and A_2B miktoarm star copolymers of aromatic polyether and PS [125]. (b) 3-arm star-shaped diblock copolymers of polyether and PS [126]. (c) 4-arm star-shaped diblock copolymers of PAES and poly(MeO_2MA-*co*-PPEGMA) [127].

4. Conclusion and future outlooks

At the dawn of the 21st century, it has become possible to synthesize a wide array of copolymers with controlled architectures like di- and triblock copolymers, graft, mikto-arm and star-block copolymers, and polymer brushes by means of reaction protocols involving consecutive steps of condensation and reversible-deactivation radical polymerizations. Numerous examples of ABA triblock copolymers with a polycondensate B block, like for instance PBT, PC, PU, PEEK, PSEK or PF, were obtained. ATRP was by far the most frequently used RDRP to grow blocks A from α,ω-telechelic polycondensate macroinitiators, and only two reported examples used either RAFT or MADIX approaches. Surface-initiated ATRP of various monomers has been often considered to grow polymer brushes from PA, PU, PES and PEEK surfaces in order to tailor their interfacial properties. Specific functionalization for antifouling or stimuli-responsive properties and control of the hydrophilic/hydrophobic character were achieved through efficient grafting and activation of ATRP initiating sites at surfaces. An important breadth of knowledge was recently brought on the controlled synthesis of rigid semi-conducting polymers like PPV and rrP3HT, PF and PPO by either non-traditional SGCP or CGCP, respectively. By performing RDRP (namely ATRP, NMP and RAFT) from the aforementioned polymers after efficient end-group modification, rod-coil block copolymers could be obtained with various microphase separated morphologies in the solid state. Hence, the control of the macromolecular characteristics of the copolymer allows the tuning of the electronic and optoelectronic properties of the materials. In solution, the behavior of different rod-coil block copolymer aggregates was also investigated.

In the future, it can be anticipated that a significant effort will be devoted to the development of next generations of semi-conducting copolymers with processability and conducting properties compatible with their integration in commercial organic electronic devices. Novel opportunities for macromolecular engineering between condensation and vinyl polymers synthesized by RDRP may be found through a more systematic implementation of "click" reactions [128] in condensation polymerizations and polycondensate-RDRP polymer coupling. For instance, recent methodologies like copper(I)-catalyzed 1,3-dipolar cycloaddition step-growth polymerization of difunctional azides and alkynes [129] or step-growth thiol-ene (photo)polymerization [130] should be advantageously envisioned and combined with RDRP strategies, including chain extension experiments or end-coupling reactions.

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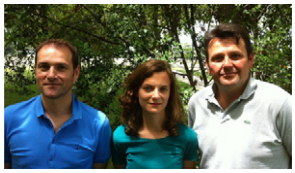

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Stéphane Mazières (right) received his Ph.D. degree in 1994 from Paul Sabatier University of Toulouse, for works on germanium chemistry performed in Professor Jacques Satgé's Laboratory. In 1995 he carried out postdoctoral research at University of Colorado at Boulder with Pr. Josef Michl, working mainly on polysilanes. In 1997 he joined Pr. Guy Bertrand's group at the LCC in Toulouse, as a postdoctoral research associate and studied some particular aspects of carbene chemistry. Since 1998 he has been Assistant Professor at the Laboratory of Fundamental and Applied Heterochemistry (LHFA) in Toulouse. In 2007 he joined Pr Mathias Destarac when he started his group at LHFA. His current research interests include hetero-atom chemistry and RAFT/MADIX polymerization.

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